California Environmental Protection Agency
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State of California
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DEPARTMENT OF PESTICIDE REGULATION
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EXECUTIVE SUMMARY
of Report EH 92-03 Entitled
"Dissipation of Methyl Parathion from Flooded Commercial Rice Fields"

Environmental Monitoring and Pest Management Branch
Department of Pesticide Regulation

PURPOSE

The Department of Pesticide Regulation's Environmental Hazards Assessment Program (EHAP) monitored methyl parathion residues to assess the adequacy of measures adopted in rice culture to reduce concentrations of this pesticide in the Sacramento River.

BACKGROUND

Methyl parathion is a pesticide with many uses in California, including rice, where it is used to control the tadpole shrimp (Triops longicaudatus). Residues, presumably from applications on rice, have been detected in water samples from the Colusa Basin Drain in the Sacramento Valley at levels that are toxic to aquatic organisms.

Water quality objectives are limits or levels of water quality constituents or characteristics which are established for the reasonable protection of beneficial uses of water or the prevention of nuisance within a specific area (Water Code Section 13050 [h]). There is no numerical water quality objective for methyl parathion. There are a number of narrative objectives, including the following:

> "Inland surface water communities and populations, including vertebrate, invertebrate, and plant species, shall not be degraded as a result of the discharge of waste" (Inland Surface Waters Plan, April, 1991).

The Central Valley Regional Water Quality Control Board has prohibited the discharge of irrigation water from rice fields containing methyl parathion unless the discharger is following a management practice, consisting of specific rice pesticide handling activities, approved by the Board. To receive approval, the management practice must be expected to meet a performance goal, defined as concentrations of water quality constituents established for receiving waters that a discharger must make best efforts to meet. They serve as a measure of success in improving water quality.

To promote dissipation and meet the performance goal, water management practices have been implemented that prohibit the

discharge of irrigation water from rice fields treated with methyl parathion until the 25th day following application.

To assess the adequacy of this mitigation measure, this study quantified concentrations of methyl parathion in water from five commercial rice fields in Glenn and Colusa counties. In addition, methyl paraoxon, a toxicologically significant degradation product, was also analyzed for in water. Studies were conducted over a 23-day period following application, allowing the dissipation half-life for methyl parathion in water to be calculated.

STUDY METHODS

Methyl parathion was applied aerially to 5 flooded commercial rice fields at the maximum label rate of 1 pint per acre. Water samples were collected from the bottom cultivated portion of each field from 2 through 5, 7, 9, 11, 15, 19, and 23 days after application.

RESULTS

The rate at which methyl parathion dissipated from rice fields was found to be higher immediately after application, when the dissipation half-life (the amount of time it takes the amount of methyl parathion to be halved) was calculated to be 1 day. Toward the end of the sampling period, the rate of dissipation had decreased. At that time the dissipation half-life was calculated to be almost 5 days.

Based on the results obtained in this study, methyl parathion concentrations applied to rice fields can be expected to reach 0.38 micrograms per liter on the 24th day after application. The 1991 performance goal for methyl parathion was 0.26 micrograms per liter, and for 1992 is 0.13 micrograms per liter.

Methyl paraoxon concentrations declined rapidly in all fields, with concentrations falling below the detection limit (0.05 µg/L) by day 9 after application in one field, and by day 7 after application in the other 4.

CONCLUSIONS

The 1992 performance goal for methyl parathion is 0.13 micrograms per liter. Despite the results of this study indicating the level in rice at the end of the holding period will be 0.38 micrograms per liter, the Regional Water Quality Control Board has approved the discharge of irrigation return flows for the 1992 season. As an extra precaution, they have required not only a prohibition of discharge of irrigation water from rice fields treated with methyl parathion until the 25th day following application, but also several other management measures to minimize discharges from rice fields.

The Department of Pesticide Regulation will continue to monitor for methyl parathion in the Sacramento River to determine whether, in view of the increased water flows and the pesticide management program in place, this rice pesticide meets the 1992 performance goal of 0.13 micrograms per liter.

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DISSIPATION OF METHYL PARATHION FROM FLOODED COMMERCIAL RICE FIELDS

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ABSTRACT

Methyl parathion (O,O-dimethyl O-4-nitrophenyl phosphorothioate) is a non-systemic insecticide and acaricide used in California rice fields to control tadpole shrimp (Triops longicaudatus). Residues have been detected in water samples from the Colusa Basin Drain in the Sacramento Valley at levels that are acutely toxic to aquatic organisms. To promote dissipation, water management practices prohibit the discharge of irrigation tailwater from rice fields treated with methyl parathion until the 25th day following application. Additional field dissipation data is needed to assess the adequacy of this mitigation measure. Although methyl paraoxon (O,O-dimethyl O-4-nitrophenyl phosphate) is not a major degradation product, field dissipation data are also needed because it is toxicologically significant. This study quantified concentrations of methyl parathion and methyl paraoxon found in water from five commercial rice fields in Glenn and Colusa counties over time, and determined the dissipation half-life for methyl parathion.

Water samples were collected from the bottom cultivated check of each field from 2 through 5, 7, 9, 11, 15, 19, and 23 days after application (DAA). Methyl paraoxon concentrations declined rapidly in all fields, with concentrations falling below the detection limit (0.05 µg/L) by 9 DAA in one field and 7 DAA in the other 4. The decline of methyl parathion concentrations followed biphasic first-order kinetics, with log-transformed concentrations proportional to DAA in each phase.

A common biphasic linear dissipation model described the five fields, and the respective phase one and phase two half-lives were 1.0 day and 4.7 days. Predicted 90th percentiles of methyl parathion concentrations in the bottom check of commercial rice fields from 0 to 24 DAA fell from 1890 to 0.38 µg/L.

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DISCLAIMER

The mention of commercial products, their source or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of product.

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INTRODUCTION

Methyl parathion (O,O-dimethyl O-4-nitrophenyl phosphorothioate) is a non-systemic, contact and stomach insecticide and acaricide. It is used in California rice fields to control tadpole shrimp (Triops longicaudatus), which damage young submerged rice seedlings with their feeding and burrowing activities. In flooded soils and aquatic systems, methyl parathion may be degraded by; photolytic or metabolic conversion to the more toxic methyl paraoxon (O,O-dimethyl O-4-nitrophenyl phosphate), chemical or enzymatic hydrolysis to p-nitrophenol and dimethyl-O-thiophosphoric acid, or enzymatic nitro-group reduction to methyl amino parathion. The hydrolysis and reduction degradation products are less toxic than the parent compound. It has been shown that the major route of degradation is through nitro-group reduction because the predominately anaerobic conditions favor reduction by bacterial populations in the soil compartment. Chemical hydrolysis and hydrolysis by bacterial populations suspended in the water compartment are minor degradation pathways (Adhya et al., 1987; Badawy & El-Dib, 1984; Crossland & Bennet, 1984; Crossland et al., 1986; Sharmila et al., 1988; Smith et al., 1978).

The majority of methyl parathion applications made to California rice fields occur in the Sacramento Valley where ninety percent of the annual rice crop is grown. In 1988, more than 40,300 pounds (18,279 kg) were applied to over 45,100 acres (18,220 ha) in Glenn and Colusa counties (California Department of Food and Agriculture, 1988). The majority of irrigation tailwater from these fields ultimately enters the Sacramento

River via the Colusa Basin Drain. The California Department of Fish and Game in cooperation with the Department of Pesticide Regulation (formerly the California Department of Food and Agriculture) and the California Regional Water Quality Control Board-Central Valley Region monitored the Sacramento River and the Colusa Basin Drain for rice pesticides during the 1990 growing season. During May and June, methyl parathion was detected in water samples from the Colusa Basin Drain at concentrations that ranged from 0.12 to 0.66 µg/L (Department of Fish and Game, 1990). These levels are acutely toxic to aquatic organisms, particularly the estuarine mysid Neomysis mercedis (Central Valley Regional Water Quality Control Board, 1989). Pursuant to the amendment of the Water Quality Control Plan for the Sacramento River, Sacramento-San Joaquin Delta and San Joaquin basins (Central Valley Regional Water Quality Control Board Resolution No. 90-028), water management practices that reduce methyl parathion concentrations in surface water must be implemented. For 1991, such practices should meet a 0.26 µg/L performance goal (daily instantaneous maximum) in all waters designated as freshwater habitat. To promote dissipation of methyl parathion, water management practices were implemented to prohibit the discharge of irrigation tailwater from rice fields until the 25th day following application (Central Valley Regional Water Quality Control Board, 1991). Additional field dissipation data are needed to assess the adequacy of this mitigation measure. Although methyl paraoxon is not a major degradation product, field dissipation data are also needed because it is toxicologically significant. The objective of this study was to quantify concentrations of methyl parathion and methyl paraoxon found in

water from commercial rice fields in Glenn and Colusa counties over time, and determine the dissipation half-life for methyl parathion.

MATERIALS AND METHODS

Study Sites

Five commercial rice fields were used to examine the dissipation rate of methyl parathion and methyl paraoxon under flooded field conditions. Fields 1, 2, 3, and 4 were located in Colusa county and had respective total areas of 15.1, 34.4, 41.8 and 36.4 ha (Fig. 1). Field 5 was located in Glenn county and had a total area of 28.3 ha. Only the bottom cultivated check of each field was used in the study. Bottom check areas and additional field characteristics are listed in Table 1.

Selection of the fields was based on representative cultural and water management practices, accessibility of the properties, and growers permission for field access. The fields had been laser-leveled and were chiseled, disced, planed and rolled prior to flooding. Irrigation tailwater was managed with conventional flow-through irrigation systems. Fields 2, 3 and 4 had fallow land adjacent to the bottom cultivated check to contain treated water spilling from the field.

An emulsifiable concentrate formulation of methyl parathion was aerially applied to flooded fields at the maximum label rate of 1 pint per acre (0.70 kg a.i./ha) for control of tadpole shrimp. Application to Fields 1 (1 May 1991) and 2 (11 May 1991) occurred 10 days after seeding, Fields 3 and 4 (17 May 1991) 12 days after seeding, and Field 5 (28 May 1991) 14 days after seeding.

Study Design and Sampling Methods

Two composite water samples were collected from the bottom cultivated check of each field from 2 through 5, 7, 9, 11, 15, 19, and 23 days after application (DAA). Each composite sample consisted of 4 subsamples collected at randomly selected sites around the perimeter of the check. On each sampling day, the mean water temperature and pH were obtained from measurements made at each subsample collection site (n=8), and the water depth in centimeters was recorded at eight previously established locations in the bottom check.

Water was collected from the bank of the check with an open 0.95-L glass jar attached to a 4.5 m aluminum extension pole. Subsamples were poured through a stainless steel funnel into narrow-neck 1-L amber glass bottles. The samples were preserved by acidifying to pH 3 with the addition of a predetermined amount of 3N hydrochloric acid. Sample bottles were then sealed with Teflon®- lined caps, placed on wet ice for transport, and stored at 4°C until analyzed.

The sampling period for Field 2 extended only through 15 DAA because water was released from the entire field into the adjacent fallow check. Similarily, Fields 3 and 4 were not sampled on 19 DAA because there was no water in the bottom check. In both fields, water from the top adjacent check subsequently entered the bottom check enabling sample collection on 23 DAA. Methyl parathion is generally applied to flooded fields. Field 5, however, was in the process of being re-flooded on 2 DAA and water had not reached the bottom check. Sampling commenced on 3 DAA when flooding was completed.

Chemical Analysis and Quality Control

The analytical method for the determination of methyl parathion and methyl paraoxon in water was developed by the California Department of Food and Agriculture, Chemistry Laboratory Services (CDFA). One-liter water samples were extracted three times by shaking in a separatory funnel with one 100 mL and two 80 mL aliquots of methylene chloride. The organic layers were filtered through anhydrous sodium sulfate and filter paper, combined in a boiling flask, and evaporated just to dryness on a steam bath. The combined extracts were transferred, brought up to final volume with acetone, and analyzed by gas chromatography (GC) using a flame photometric detector. The minimum detectable limit was 0.05 µg/L. The extraction procedure and the GC operating conditions are described in Appendix I. Method validation was conducted prior to and independent of the field study. Water samples were spiked in triplicate with methyl parathion at 0.1, 1.0, 10, 100, 500, and 1500 µg/L or methyl paraoxon at 0.1, 1.0, 10, and 100 µg/L and analyzed to determine the method percent recovery. The mean percent recoveries were 99 $\pm$ 8.8 (n=18) and 104 $\pm$ 7.03 (n=12) for methyl parathion and methyl paraoxon, respectively (see Appendix II, Tables II-1 and II-2).

Quality control procedures for methyl parathion and methyl paraoxon analyses included storage stability tests conducted prior to the field study, intralaboratory continuing quality control analyses, and interlaboratory analyses of split water samples. Storage stability was examined with water samples refrigerated at pH 3 and 8.5. Duplicate water samples were spiked with 20 µg/L methyl parathion or methyl paraoxon and analyzed after 0, 2, 4, 8, 10, and 14 days. There was no

appreciable loss of methyl parathion at pH 3 and 8.5, and methyl paraoxon at pH 3 during the storage period (see Appendix, Tables II-3 through II-6). The mean recovery of methyl paraoxon at pH 8.5 was 70% after 2 days and 55% after 4 days. Field samples were extracted within 3 days after sample collection, therefore storage stability under pH 3 was not in question. Continuing quality control analyses at CDFA and Enseco-Cal (CAL), the quality control laboratory, included one blank and one spiked water sample analyzed with each extraction set (1 to 10 samples), and blind-spike samples (see Appendix II, Tables II-7 through II-10).

Statistical Methods

The SAS® General Linear Models and Regression procedures were used for the statistical analysis of data (SAS® Institute, 1987). SAS® is a registered trademark of SAS® Institute, Inc., Cary, NC, USA.

SAS® Regression procedures were used to characterize dissipation in individual fields, and determine if there was a common model. Using a biphasic linear model, analyses were conducted for each field separately to relate both log-transformed concentrations and masses of methyl parathion to DAA. The join point of the two phases at 9 DAA was determined by examination of plots of the log-transformed data.

To determine if the biphasic linear trends over time were parallel, log concentrations and masses from all fields at 3, 4, 5, 7, 9, 11, and 15 DAA were then analyzed by repeated measures analysis of variance (ANOVA) using SAS® General Linear Models procedures. "Fields" were used as

replicates, DAA as the repeated factor, and the analysis included only the DAA with data for all 5 fields. The data were analyzed by this method because the same fields were measured every time (DAA), as opposed to an independent sample of fields at each DAA (Littel, 1989; Myers, 1972). The repeated measures ANOVA in effect removes differences in mean level between fields, and tests whether the time trends for the fields are parallel. The interaction of DAA and "Fields" serves as the error term for the time effect.

To predict concentrations and masses in fields using the biphasic linear model, SAS® Regression procedures were used to fit the model to all the data without the "Field" terms included in the repeated measures ANOVA. The repeated measures ANOVA removes mean differences between fields. To determine how well the biphasic linear model can predict field concentrations, field differences are reabsorbed into the error variance. A SAS® program for the unbiased back-transformation of predicted log concentrations or masses (Powell, 1991) was used following this regression. Back-transformation is necessary because the regression model fit to the transformed data predicts log concentration at any given DAA. The antilog of this value underestimates the resulting predicted value. The program back-transformed predicted concentrations or masses from the regression for 0 through 24 DAA. Values at 0, 1, and 24 DAA were extrapolated because no sampling occurred on these days. The methyl parathion dissipation half-life for each phase was then estimated as the earliest day at which the back-transformed predicted concentration or mass was less than or equal to one-half the predicted value at 2 DAA and 9 DAA. Finally, the 90th percentile of methyl parathion concentration

and mass (MP_{90th}) in rice fields on each DAA from 0 to 24 were calculated from the expression:

$$MP_{90th} = \exp [\ln MP + t_{(.90,\ 39 \text{ deg. of f.})} \cdot (\text{Root MSE})],$$

where ln MP is the predicted log value, $t_{(.90,\ 39 \text{ deg. of f.})}$ is the 90th percentile of the t distribution, and Root MSE is the root mean squared error for all fields over all days sampled.

RESULTS AND DISCUSSION

Quality Assurance/Quality Control

On 2, 4, 7, and 11 DAA, the first composite sample was split into two 1-L aliquots and analyzed for methyl parathion and methyl paraoxon by CDFA and CAL. Results of the split sample analyses (see Appendix II, Tables II-11 and II-12) were analyzed by linear regression for interlaboratory comparison. The intercept from 18 pairs of regressed methyl parathion concentrations was not significantly different from 0 ($p = 0.5174$); the slope, however, was significantly different from 1 ($p = 0.001$) indicating a bias. For 13 pairs of data, methyl parathion concentrations reported by CAL were 1 to 11% higher than CDFA's. The higher concentrations may be due to the different analytical method used by CAL. The mean percent recovery for continuing quality control was 101 $\pm$ 9.02 (n=12); CDFA reported a mean percent recovery of 95 $\pm$ 2.8 (n=18). The regression of 8 pairs of methyl paraoxon concentrations showed no pattern of correlation between the two laboratories (model $p = 0.1647$, Adjusted R-square = 0.177). At this time, the reason for this result is not known.

Field Data

Field conditions recorded during the sampling periods are summarized in Table 2. Fields 1 and 2 had mean water pH values of 7.2, whereas Fields 3, 4, and 5 were more basic. Badawy and El-Dib (1984) found that the hydrolysis rate of methyl parathion in aquatic solutions increased under alkaline conditions. The difference in pH was not expected to result in different dissipation rates among the fields because hydrolysis is a minor degradation pathway. The large differences in minimum and maximum water temperature were correlated with the time of day sampling occurred. Water depths generally declined over the sampling periods. Water flowing from the top adjacent check caused an increase in the water depth on 9 DAA in Field 2, and on 11 and 19 DAA in Field 5. Increases were also recorded on 23 DAA in Fields 1 and 4. To account for variable water depths, data were also analyzed with methyl parathion concentrations normalized to kg/ha ("mass").

Complete field data and the analytical results are listed in Appendix III. Methyl paraoxon rapidly dissipated in all fields with concentrations falling below the 0.05 µg/L detection limit by 9 DAA in Field 1, and 7 DAA in Fields 2, 3, 4 and 5. These data were not statistically analyzed. Methyl parathion and methyl paraoxon concentrations reported for Field 1 at 2 DAA are questionable because of likely contamination during the blow down step of the analytical method. These data, therefore, were not used in the statistical analyses.

Data Analysis

The dissipation of methyl parathion from the 5 individual fields followed biphasic first-order kinetics with both logarithmic concentration and mass proportional to DAA in each phase. This implies that the variable water depths did not affect the decline over time. Examination of plots of log-transformed concentrations and masses for individual fields suggested that the join point of the two phases was at 9 DAA, but there were overall level differences between fields. Phase one slopes ranged from 0.42 to 0.97 and 0.49 to 1.04 with concentrations and masses, respectively. Phase two slopes ranged from 0.07 to 0.30 with concentrations, and from 0.15 to 0.37 with masses. A biphasic process is one in which the reaction sequence for the breakdown of substance A to product C consists of two steps occurring in series. Substance B is the product in the first step and the reactant in the second step (Espenson, 1981):

$$A \xrightarrow{k} B \xrightarrow{k'} C$$

A plot of transformed concentrations of A versus time yields two sequential straight-line segments. The reaction sequence for the degradation of methyl parathion (MP) to products (P, P') may be described by consecutive first-order reactions representing (1) nitro-group reduction, the major route of dissipation, followed by (2) hydrolysis, the minor dissipation route:

$$(1)\quad MP \xrightarrow{k} P$$

$$(2)\quad MP \xrightarrow{k'} P'$$

The reaction rate for the disappearance of methyl parathion over time (-d[MP]/dt) can be expressed as:

$$-d[MP]/dt = k[MP] + k'[MP]$$

Integration and rearrangement of this equation yields:

$$\ln [MP] = \ln [MP]_i - kt - k't',$$

where $\ln [MP]_i$ is the initial transformed methyl parathion concentration. Regression analyses using the above model with 2 through 9 DAA as the time factor, t, and 9 through 23 DAA as the time factor, t', resulted in adjusted R-square values of 0.99, 0.95, 0.99, 0.99, and 0.98 with concentrations, and 0.99, 0.93, 0.99, 0.99, and 0.96 with masses.

The significant biphasic time effect in the repeated measures ANOVA (Table 3) showed that the fields had parallel biphasic trends over time for both log concentration and mass; that is, all fields can be described by a common dissipation rate.

While dissipation occurred at the same rate in all fields, the actual concentrations varied. To determine how well concentration or mass in a field on any DAA could be predicted, regression analyses were conducted to fit the biphasic linear model to both daily field concentrations (Fig. 2) and masses. The equations resulting from these analyses were:

$$\ln \text{Concentration} = 6.363 - 0.697(DAA) - 0.150(DAA') \text{ and}$$

$$\ln \text{Mass} = -0.140 - 0.762(DAA) - 0.172(DAA'),$$

where DAA is the time factor from 0 through 9 DAA and DAA' is the time factor from 9 DAA through 24 DAA. The two estimated parameters in each equation represent the slopes of the two phases of the model. Back-transformed predicted concentrations for 0 through 24 DAA dropped from 806 to 0.15 µg/L, with concentrations falling below the 1991 performance goal at 21 DAA (Table 5). Dissipation half-lives for phase one and

phase two were estimated at 1.0 day and 4.7 days, respectively. Normalizing concentrations to kg/ha did not appear to make a difference in the estimated half-lives. Back-transformed predicted masses dropped from 1.40818 to 0.00010 kg/ha (Table 5), with phase one and phase two half-lives estimated at 0.9 day and 4.0 days, respectively.

The biphasic linear trend over time and the associated dissipation half-life estimates reported here were different from what has been reported in the literature. The decline of methyl parathion in flooded soil or aquatic systems has been shown to proceed by single-phase first-order kinetics (Adhya et al., 1987; Dortland, 1980; Seiber & McChesney, 1987; Sharmila et al., 1988; Van Veld & Spain, 1983). In these studies, half-life estimates for microbial degradation were approximately one to five days longer than the phase one half-life reported here (Table 6). All but one of these studies, however, were conducted under laboratory conditions and may not be indicative of dissipation under field conditions. The study conducted outdoors under flooded rice culture reported a longer half-life of 1.8 day for the decline of methyl parathion (Seiber & McChesney, 1987). Because only one field was included in this study, comparison of estimated half-lives is problematic.

The 90th percentile of methyl parathion concentration and mass from 0 to 24 DAA fell from 1890 to 0.38 µg/L and 3.63829 to 0.00029 kg/ha, respectively (Table 5). These levels reflect an upper limit only. On any given DAA, 90% of commercial rice fields would be expected to have an equal or lesser concentration in the bottom check. Irrigation tailwater released on 24 DAA would have methyl parathion concentrations less than

released on 24 DAA would have methyl parathion concentrations less than or equal to 0.38 µg/L.

CONCLUSIONS

The dissipation of methyl parathion over time followed biphasic first-order kinetics with respective phase one and phase two half-lives of 1.0 day and 4.7 days. The 90th percentiles of methyl parathion concentrations from 0 to 24 DAA fell from 1890 to 0.38 µg/L.

Figure 1. Locations of five commercial rice fields in Glenn and Colusa counties.

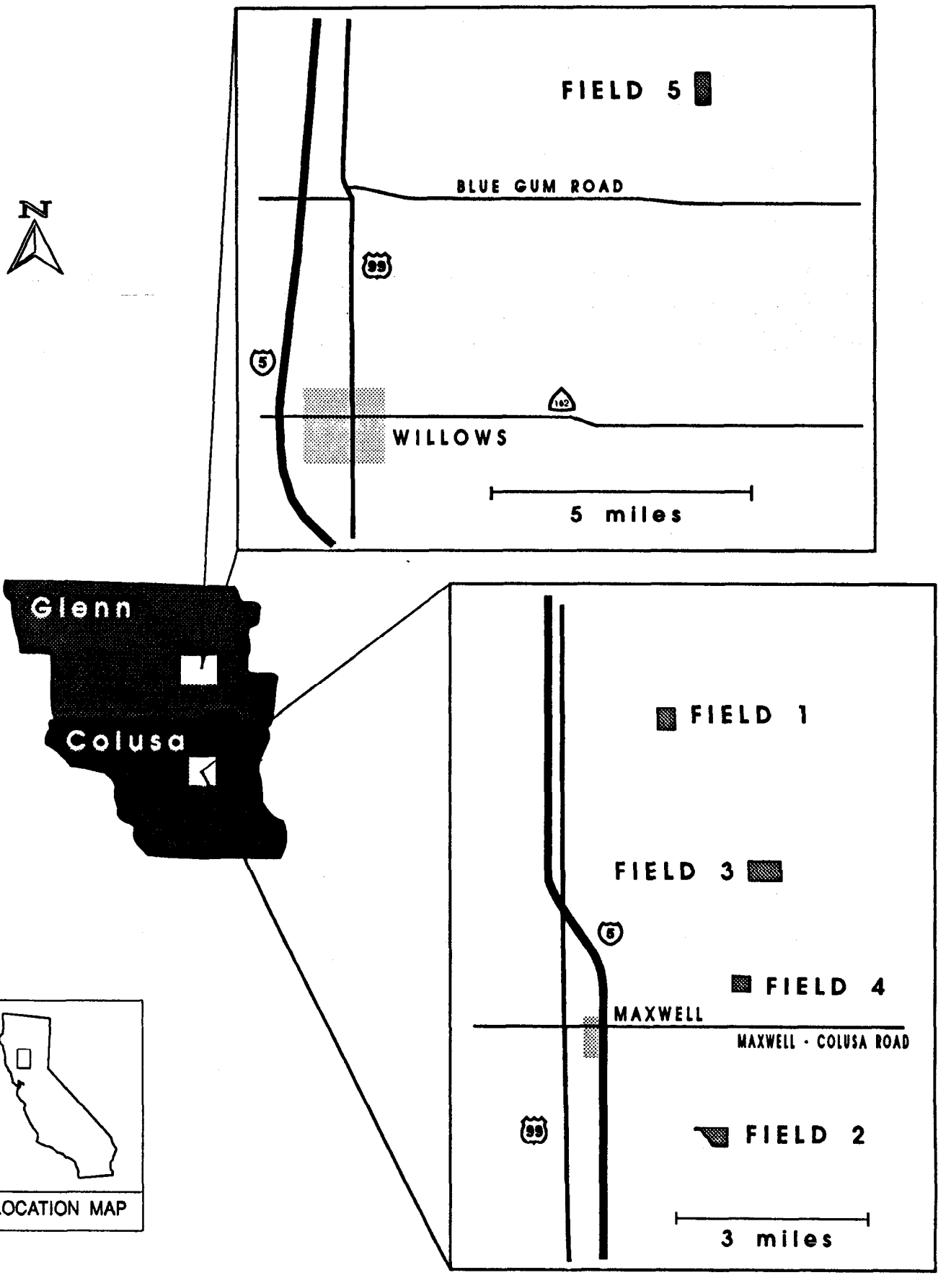

Figure 2. Predicted and actual methyl parathion concentration versus day after application.

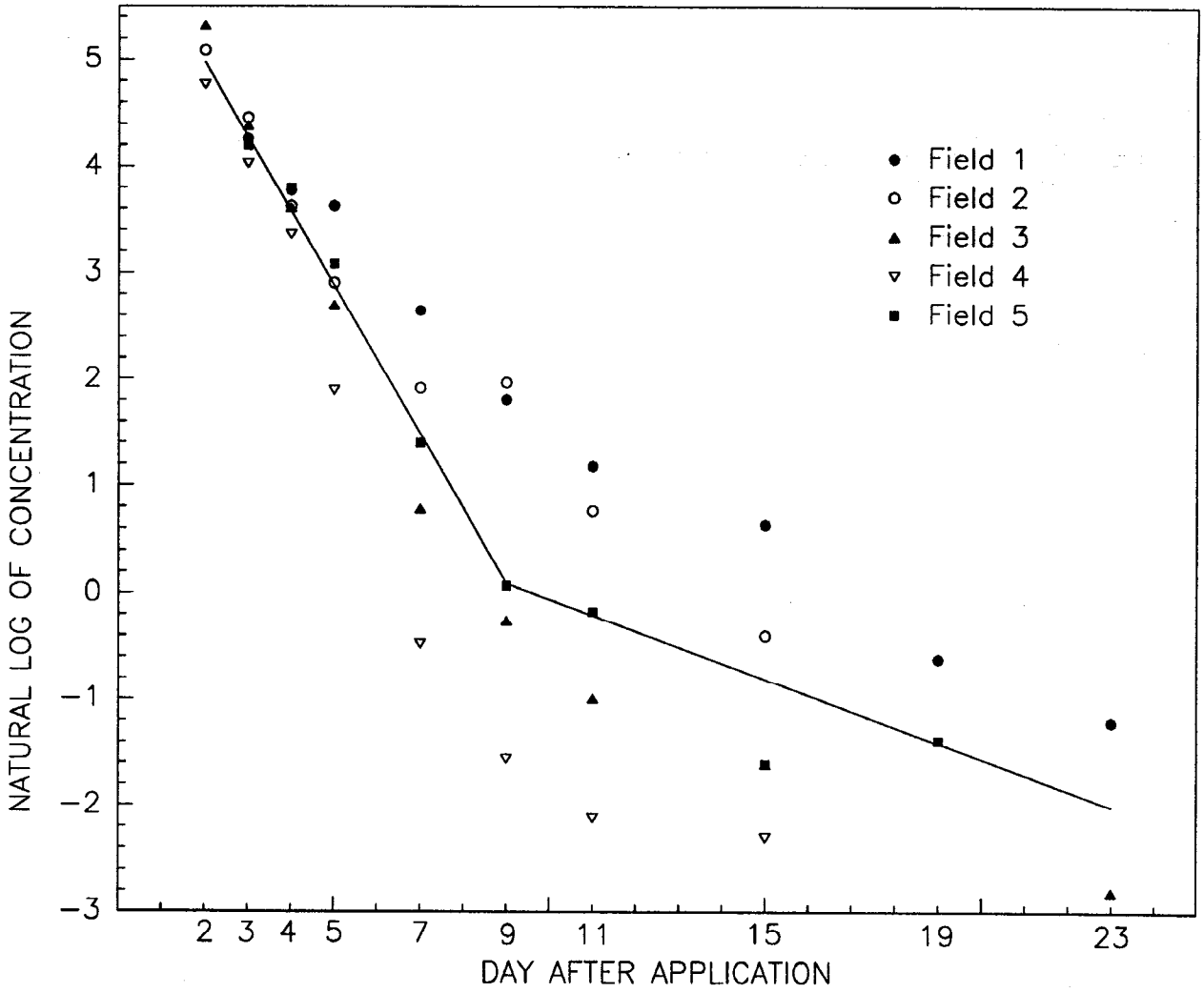

Table 1. Characteristics of five commercial rice fields in Glenn and Colusa counties.

Field	Bottom Check Area (ha)	Soil Type	% Soil Organic Matter	Rice Cultivar
1	2.1	Wekoda silty clay (Aquic Chromoxererts) 4% sand/51% silt/45% clay	1.0	M 401[a] Seed rice
2	2.2	Wekoda silty clay (Aquic Chromoxererts) 4% sand/51% silt/45% clay	0.5	M 202[b] Paddy rice
3	5.1	Wekoda silty clay (Aquic Chromoxererts) 4% sand/51% silt/45% clay	1.0	M 202 Seed rice
4	2.3	Wekoda silty clay (Aquic Chromoxererts) 4% sand/51% silt/45% clay	1.0	M 202 Paddy rice
5	1.8	Sunnyvale Clay (Typic Calciaquoll) 14% sand/40% silt/47% clay	1.0	M 202 Paddy rice

a - Medium grain, late maturity.
b - Medium grain, early maturity.

Table 2. Sampling periods during 1991 and the water pH, water temperature, and water depth in the bottom check of five commercial rice fields.

Variable	Field 1	Field 2	Field 3	Field 4	Field 5
Sampling period	5/2-5/23	5/13-5/26	5/19-6/9	5/19-6/9	5/31-6/23
pH					
Maximum	7.5	8.1	8.6	9.4	8.2
Minimum	6.8	6.9	7.4	7.8	7.6
Mean	7.2	7.2	7.9	8.4	7.8
Std	0.23	0.39	0.35	0.49	0.18
	(n=10)	(n=8)	(n=9)	(n=9)	(n=9)
Water temp., °C					
Maximum	30.3	34.1	33.5	29.3	28.2
Minimum	12.4	13.0	15.9	19.0	17.6
Mean	18.3	22.5	24.1	24.4	23.1
Std	4.75	7.39	5.32	3.96	3.40
	(n=10)	(n=8)	(n=9)	(n=9)	(n=9)
Water depth, cm					
Maximum	19.2	9.0	13.8	11.8	14.1
Minimum	8.8	4.3	3.9	3.3	5.3
Mean	14.7	6.85	10.7	8.5	9.3
Std	3.86	1.84	3.33	2.86	2.84
	(n=6)	(n=8)	(n=8)	(n=8)	(n=8)

Table 3. Repeated measures analysis of variance on transformed methyl parathion concentrations and masses for testing the biphasic linear trend over time (DAA, days after application) in 5 commercial rice fields.

Source of Variation	Degrees of Freedom	Sum of Squares	F-Value	P-Value
		Concentration		
Fields	4	19.80		
DAA				
Biphasic linear	2	123.68	61.2	<0.001
Other	4	0.69	2.87	0.05<p<0.10
Fields x DAA				
Fields x Biphasic	8	8.09		
Fields x Other	16	0.96		

Summary (n=5):

DAA	Mean (µg/L)	Std. Dev.
3	71.95	11.801
4	38.22	6.347
5	19.81	11.368
7	8.24	8.138
9	3.06	3.284
11	1.34	1.320
15	0.61	0.748

		Mass		
Fields	4	28.53		
DAA				
Biphasic linear	2	157.62	69.3	<0.001
Other	4	0.47	0.86	>0.25
Fields x DAA				
Fields x Biphasic	8	9.09		
Fields x Other	16	2.18		

Summary (n=5):

DAA	Mean (kg/ha)	Std. Dev.
3	0.0884	0.03018
4	0.0431	0.02203
5	0.0263	0.02278
7	0.0077	0.01083
9	0.0031	0.00363
11	0.0013	0.00170
15	0.0005	0.00079

Table 4. Analysis of variance for regression analyses to fit the biphasic linear model to transformed methyl parathion concentrations and masses.

Source of Variation	Degrees of Freedom	Sum of Squares	F-Value
		[a] Concentration	
Biphasic linear trend	2	198.173	120.515
Error	39	32.065	
		[b] Mass	
Biphasic linear trend	2	241.789	100.151
Error	39	47.077	

a - Adjusted R-squared = 0.854
b - Adjusted R-squared = 0.829

Table 5. Back-transformed predicted methyl parathion concentrations (Pred. MP conc.) and masses (Pred. MP mass), and predicted 90th percentile concentrations and masses (MP_{90th}).

	a DAA	b Pred. MP conc. (µg/L)	c MP 90th (µg/L)	b Pred MP mass (kg/ha)	c MP 90th (kg/ha)
	0	806	1890	1.40818	3.63829
	1	410	941	0.67707	1.69727
	2	208	469	0.32365	0.79178
phase	2.9	112	250	0.16574	0.39864
one	3	105	233	0.15381	0.36937
	4	52.6	116	0.07268	0.17231
	5	26.3	57.9	0.03414	0.08038
	6	13.1	28.8	0.01595	0.03750
	7	6.52	14.4	0.00741	0.01749
	8	3.22	7.16	0.00342	0.00816
join point-->	9	1.59	3.56	0.00157	0.00381
	10	1.38	3.07	0.00133	0.00320
	11	1.19	2.64	0.00113	0.00270
	12	1.03	2.27	0.00096	0.00227
	13	0.89	1.96	0.00081	0.00191
phase	13.7	0.80	1.76	0.00071	0.00169
two	14	0.76	1.69	0.00068	0.00161
	15	0.65	1.45	0.00057	0.00135
	16	0.56	1.25	0.00047	0.00114
	17	0.48	1.08	0.00040	0.00096
	18	0.41	0.93	0.00033	0.00081
	19	0.35	0.80	0.00027	0.00068
	20	0.30	0.69	0.00023	0.00057
	21	0.25	0.59	0.00019	0.00048
	22	0.21	0.51	0.00015	0.00041
	23	0.18	0.44	0.00013	0.00034
	24	0.15	0.38	0.00010	0.00029

a - Day after application. Concentrations at 0, 1, and 24 DAA are extrapolated. No sampling occured on these days.

b - Back-transformed from predicted log values (Powell, 1990).

c - The predicted 90th percentile concentrations and masses were calculated from the expression:

$$MP_{90th} = \exp[\text{pred. ln MP} + t_{(.90,\ 39\ d.f.)} \cdot (\text{Root MSE})],$$

where ln MP is the predicted log value, Root MSE (root mean squared error) is 0.90675 for concentrations and 1.09869 for masses, and $t_{(.90,\ 39\ d.f.)} = 1.303$.

Table 6. Half-lives of the single-phase first-order dissipation of methyl parathion in flooded soils and aquatic systems reported in the literature.

Half-life (Days)	Reference	Conditions
1.8	Seiber & McChesney, 1987	1
3.2	Van Veld & Spain, 1983	2
3.25	Dortland, 1980	3
3.58	Adhya et al., 1987	4
4.13	Dortland, 1980	5
4.17	Adhya et al., 1987	6
5.17	Sharmila et al., 1988	7
5.44	Adhya et al., 1987	8
5.5	Adhya et al., 1987	9

1. Flooded rice field, pH 7, 27°C.
2. Intact sediment-water core, 18°C.
3. Aquarium (water, sediment, aquatic vegetation), pH 7.4.
4. Incubation study with flooded Pokkali soil, pH 7.2, 28°C.
5. Aquarium (water, sediment, aquatic vegetation), pH 7.7.
6. Incubation study with flooded Alluvial soil, pH 6.8, 28°C.
7. Incubation study with flooded Alluvial soil, 25°C.
8. Incubation study with flooded Kari soil, pH 6.8, 28°C.
9. Incubation study with flooded Sukinda soil, pH 7.1, 28°C.

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APPENDIX I

Laboratory Analytical Methods

CALIFORNIA DEPT. OF FOOD & AGRIC.
CHEMISTRY LABORATORY SERVICES
ENVIRONMENTAL MONITORING SECTION
3292 Meadowview Road
Sacramento, Ca. 95832
(916) 427-4649/4999

Original Date: 06/09/89
Supercedes: New
Current Date: 07/02/91
Method #:

METHYL PARATHION AND METHYL PARAOXON IN RICE DRAIN WATER

SCOPE:

This method is for the determination of Methyl Parathion and Methyl Paraoxon in rice drain water.

PRINCIPLE:

The samples of water were extracted by shaking in a separatory funnel with methylene chloride. The extract was filtered and evaporated to dryness. It was then transferred and brought up to final volume with acetone. The extract was analyzed by gas chromatography using a flame photometric detector (FPD).

REAGENTS AND EQUIPMENT:

Methylene chloride and acetone (pesticide residue grade)
Sodium sulfate (anhydrous)
Steam bath (Precision Scientific Inc.)
Nitrogen evaporator (Organomation Model # 12)
Vortex mixer for test tubes
Balance (Mettler PC 4400)

ANALYSIS:

1) Remove samples from refrigerated storage and allow them to come to room temperature. Samples consist of approximately 1 L and are stored in 1 L amber glass bottles to prevent any photodegradation from occurring.

2) Record weight of the sample by weighing sample bottle before and after transfer.

3) Extract sample by shaking with 100 mL of methylene chloride for 2 min. Pressure builds up during extraction so venting is necessary.

4) Allow layers to separate and filter the organic layer through 25 g anhydrous sodium sulfate and filter paper. Collect extract in a 500 mL boiling flask.

5) Repeat steps 3 & 4 two more times using 80 mL of methylene chloride each time.

6) Rinse sodium sulfate with 20 mL additional methylene chloride and collect in the same 500 mL boiling flask.

7) Take extract just to dryness on a steam bath. Add 1-2 mL acetone to the flask to rinse down the sides.

8) Transfer extract to a graduated test tube. Rinse flask 3 times each with 2 mL of acetone. Transfer each wash to the same graduated test tube.

9) Place extract in a nitrogen evaporator with waterbath set at 35°C and evaporate to a final volume of 1 mL under a gentle stream of nitrogen.

10) Stopper the graduated test tube and mix contents by placing on a vibrating mixer for about 15 seconds. Submit sample for gas chromatographic analysis.

EQUIPMENT CONDITIONS:

Shimadzu: GC-14 A with FPD "P mode"
Column: HP-17 (50% phenol methyl silicone) 10 m x 0.53 mm x 2.0 um
Carrier gas: Helium, Flow rate: 20 mL/min
Injector: 230°C
Detector: 260°C
Temperature Program: Initial temp: 170°C held for 1 minute
Rate: 10°C/minute
Final temp: 220°C held for 4 minutes
Injection volume: 2 uL
Retention times: Methyl Parathion 3.53 ± 0.1 min. Methyl Paraoxon 3.12 ± 0.1 min.

Varian: 3700 GC WITH FPD "P mode"
Column: DB-210 (50% tri-fluoropropyl methyl polysiloxane) 15 m x 0.537 mm x 1.0 um
Carrier gas: Helium, Flow rate: 17 mL/min
Injector: 220°C
Detector: 250°C
Temperature: 190°C isothermal
Injection volume: 2 uL
Retention times: Methyl Parathion 1.38 ± 0.1 min. Methyl Paraoxon 1.80 ± 0.1 min.

CALCULATIONS:

PPB Methyl Parathion and Methyl Paraoxon

$$\text{ppb in sample} = \frac{(\text{peak height sample})(\text{ng/uL std})(\text{uL injected std})(\text{final volume mLs})(1000)}{(\text{peak height std})(\text{uL injected sample})(\text{weight of sample g})}$$

RECOVERIES:

% Recoveries of Methyl Parathion and Methyl Paraoxon

Levels	Methyl Parathion (Mean)	(SD)	Methyl Paraoxon (Mean)	(SD)
0.1 ppb (n=3)	103	15.4	113	5.77
1.0 ppb (n=3)	97	1.7	101	5.57
10.0 ppb (n=3)	96	3.1	99	1.0
100 ppb (n=3)	99	1.5	102	4.36
500 ppb (n=3)	97	5.5	---	---
1000 ppb (n=3)	102	5.03	---	---

Recovery validation was done prior to samples.

MINIMUM DETECTABLE LEVEL:

The minimum detectable level was 0.05 ppb with the S/N=3.

DISCUSSION:

Since levels varied widely, contamination was a real concern. One source of contamination was the rotary evaporator so a steam bath was used. The The nitrogen blow down apparatus used disposable pipet tips which were changed after every sample to reduce the chance of cross contamination.

REFERENCE:

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.....

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APPENDIX II

Quality Assurance Results

Table II-1. Method validation data (% recoveries) for the methyl parathion field studies.

Study: 107/108
Analyte: Methyl parathion
MDL: 0.05 ppb
Date of Report: 4/13/91

Sample Type: Surface Water
Lab: CDFA
Chemist: Jane White

Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
1821	0.13	0.1	130			
1837	0.09	0.1	89			
1856	0.09	0.1	93	104	22.6	21.7
1822	0.96	1.0	96			
1836	0.99	1.0	99			
1857	0.96	1.0	96	97	1.7	1.8
1823	9.96	10	99			
1836	9.28	10	93			
1858	9.73	10	97	96	3.1	3.2
1824	100.80	100	101			
1834	99.48	100	99			
1859	98.39	100	98	99	1.5	1.5
1825	486.00	500	97			
1833	513.00	500	103			
1860	459.00	500	92	97	5.5	5.7
1826	1448.00	1500	97			
1832	1544.00	1500	103			
1861	1608.00	1500	107	102	5.03	4.92
			OVERALL:	99	8.8	8.8

$\bar{X}$	SD	LWL	UWL	LCL	UCL
99	8.8	90	108	81	117

Table II-2. Method validation data (% recoveries) for the methyl parathion field studies.

Study: 107/108
Analyte: Methyl paraoxon
MDL: 0.05 ppb
Date of Report: 4/13/91

Sample Type: Surface Water
Lab: CDFA
Chemist: Jane White

Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
1817	0.11	0.1	110			
1831	0.12	0.1	120			
1862	0.11	0.1	110	113	5.77	5.09
1818	1.00	1.0	100			
1830	0.96	1.0	96			
1863	1.07	1.0	107	101	5.57	5.51
1819	9.81	10	98			
1829	10.01	10	100			
1864	9.88	10	99	99	1.0	1.0
1820	96.72	100	97			
1828	104.85	100	105			
1865	103.63	100	104	102	4.36	4.27
			OVERALL:	104	7.03	6.77

$\bar{X}$	SD	LWL	UWL	LCL	UCL
102	7.03	95	109	88	116

LWL/UWL (lower warning limit/ upper warning limit) = mean +/- SD
LCL/UCL (lower control limit/ upper control limit) = mean +/- 2 SD

Table II-3. Storage dissipation data for the methyl parathion field studies (refrigerated at pH 3).

Study: 107/108
Analyte: Methyl parathion
Detection Limit: 0.05 ppb
Date: 4/23/91

Sample Type: Surface Water
Lab: CDFA
Chemist: Jane White

Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV %
1638	0	3/25/91	3/26/91	19.1	20	95			
1639	0	3/25/91	3/26/91	17.6	20	88	92	4.9	5.4
1695	2	3/27/91	4/1/91	18.38	20	92			
1696	2	3/27/91	4/1/91	18.46	20	92	92	0.0	0.0
1709	4	3/29/91	3/29/91	19.69	20	98			
1710	4	3/29/91	3/29/91	19.56	20	98	98	0.0	0.0
1728	8	4/2/91	4/2/91	18.63	20	93			
1729	8	4/2/91	4/2/91	19.69	20	98	96	3.5	3.7
1800	10	4/4/91	4/9/91	19.94	20	99			
1801	10	4/4/91	4/9/91	20.04	20	100	100	0.7	0.7
1844	14	4/8/91	4/9/91	19.81	20	99			
1845	14	4/8/91	4/9/91	19.86	20	99	99	0.0	0.0

Table II-4. Storage dissipation data for the methyl parathion field studies (refrigerated at pH 8.5).

Study: 107/108
Analyte: Methyl parathion
Detection Limit: 0.05 ppb
Date: 4/23/91

Sample Type: Surface Water
Lab: CDFA
Chemist: Jane White

Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV %
1640	0	3/25/91	3/26/91	17.03	20	85			
1641	0	3/25/91	3/26/91	19.04	20	95	90	7.1	7.9
1697	2	3/27/91	4/1/91	17.85	20	89			
1698	2	3/27/91	4/1/91	19.27	20	96	93	4.9	5.4
1712	4	3/29/91	3/29/91	18.39	20	92			
1711	4	3/29/91	3/29/91	19.45	20	97	95	3.5	3.7
1730	8	4/2/91	4/2/91	17.63	20	88			
1731	8	4/2/91	4/2/91	18.86	20	94	91	4.2	4.7
1802	10	4/4/91	4/9/91	18.94	20	95			
1803	10	4/4/91	4/9/91	18.53	20	93	94	1.4	1.5
1846	14	4/8/91	4/9/91	19.51	20	98			
1847	14	4/8/91	4/9/91	18.01	20	90	94	5.7	6.0

Table II-5. Storage dissipation data for the methyl parathion field studies (refrigerated at pH 3).

Study: 107/108	Sample Type: Surface Water
Analyte: Methyl paraoxon	Lab: CDFA
Detection Limit: 0.05 ppb	Chemist: Jane White
Date: 4/23/91	

Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV %
1634	0	3/25/91	3/26/91	19.30	20	97			
1635	0	3/25/91	3/26/91	18.75	20	94	96	2.1	2.2
1699	2	3/27/91	4/1/91	19.69	20	98			
1700	2	3/27/91	4/1/91	20.00	20	100	99	1.4	1.4
1713	4	3/29/91	4/1/91	20.43	20	102			
1714	4	3/29/91	4/1/91	20.00	20	100	101	1.4	1.4
1732	8	4/2/91	4/2/91	19.43	20	97			
1733	8	4/2/91	4/2/91	19.15	20	96	97	0.7	0.7
1804	10	4/4/91	4/9/91	19.86	20	99			
1805	10	4/4/91	4/9/91	21.00	20	110	105	7.8	7.4
1848	14	4/8/91	4/9/91	20.34	20	102			
1849	14	4/8/91	4/9/91	19.82	20	99	101	2.1	2.1

Table II-6. Storage dissipation data for the methyl parathion field studies (refrigerated at pH 8.5).

Study: 107/108	Sample Type: Surface Water
Analyte: Methyl paraoxon	Lab: CDFA
Detection Limit: 0.05 ppb	Chemist: Jane White
Date: 4/23/91	

Lab Sample #	Day	Date Extracted	Date Analyzed	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV %
1636	0	3/25/91	3/26/91	20.74	20	104			
1637	0	3/25/91	3/26/91	18.02	20	90	97	9.9	10.2
1701	2	3/27/91	4/1/91	14.54	20	72			
1702	2	3/27/91	4/1/91	13.33	20	67	70	3.5	5.1
1715	4	3/29/91	4/1/91	11.29	20	56			
1716	4	3/29/91	4/1/91	10.64	20	53	55	2.1	3.9
1734	8	4/2/91	4/2/91	5.9	20	30			
1735	8	4/2/91	4/2/91	5.94	20	30	30	0.0	0.0
1806	10	4/4/91	4/9/91	4.52	20	23			
1807	10	4/4/91	4/9/91	4.31	20	22	23	0.7	3.1
1850	14	4/8/91	4/9/91	1.21	20	6			
1851	14	4/8/91	4/9/91	1.25	20	6	6	0.0	0.0

Table II-7. Continuing quality control data for the methyl parathion field study.

Study: 107
Analyte: Methyl parathion
MDL: 0.05 ppb
Date of Report: 7/10/91

Sample Type: Surface Water
Lab: CDFA
Chemist: Jane White

Extraction Set Sample No.'s	Lab #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
1001, 1003, 1037	2221	0.36*	0.1	360			
1004, 1005, 1006, 1008	2226	0.96	1.0	96			
1009, 1010	2224	0.93	1.0	93			
1011, 1015	2270	0.91	1.0	91			
1017, 1019	2292	0.97	1.0	97			
1021, 1025, 1040	2383	1.00	1.0	100			
2005	2436	0.99	1.0	99			
1027, 1029, 2007, 2009, 2011 2015, 2017, 2019, 2037	2527	4.66	5.0	93			
2021, 2025, 2049, 3001, 3005, 4001, 4005	2555	4.49	5.0	90			
1031, 1033, 2027, 2029 3007, 3009, 4007, 4009	2558	0.97	1.0	97			
2031, 2035, 3011, 3015, 3017 3019, 4011, 4015, 4017, 4019	2628	4.73	5.0	95			
1041, 1043, 2039, 2041, 3021 3025, 3027, 3029, 4021, 4025 4027, 4029	2632	0.92	1.0	92			
3031, 3035, 3037, 3039, 4031 4035, 4037, 4039, 5001, 5003 5005, 5009, 5011, 5013	2693	0.93	1.0	93			
5015, 5019	2709	0.96	1.0	96			
3041, 3043, 4041, 4043, 5021 5023, 5025, 5029	2822	0.91	1.0	91			
5031, 5033	2829	0.94	1.0	94			
5035, 5037	2853	0.94	1.0	94			
5039, 5041	2925	4.78	5.0	96			
				OVERALL:	95	2.8	3.0

* Spike recovery high due to contamination in rotary evaporator, not included in mean.

Table II-8. Continuing quality control data for the methyl parathion field study.

Study: 107
Analyte: Methyl paraoxon
MDL: 0.05 ppb
Date of Report: 7/10/91

Sample Type: Surface Water
Lab: CDFA
Chemist: Jane White

Extraction Set Sample No.'s	Lab #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
1001, 1003, 1037	2222	0.11	0.1	110			
1011, 1015	2270	1.02	1.0	102			
1021, 1025, 1040	2384	1.04	1.0	104			
2001, 2005	2439	1.08	1.0	108			
				OVERALL:	106	3.65	3.44

Table II-9. Continuing quality control data (duplicate matrix spikes) for the methyl parathion field study.

Study: 107
Analyte: Methyl parathion
MDL: 0.05 ppb
Date of Report: 7/10/91

Sample Type: Surface Water
Lab: Enseco- Cal Analytical
Chemist: Calvin Tanaka

Extraction Set Sample No.'s	Lab #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
1002, 1038	58126	0.53	0.50	107			
		0.57	0.50	114	111	4.95	4.48
1013	58232	0.42	0.50	85			
		0.48	0.50	96	91	7.8	8.6
2013, 2038	58383	0.55	0.50	111			
		0.55	0.50	111	111	0.0	0.0
3033, 4023, 4033	58577	0.48	0.50	96			
		0.46	0.50	92	94	2.8	3.0
2023, 3003, 4003	58446	0.50	0.50	101			
		0.52	0.50	104	103	2.12	2.07
5007	58676	0.46	0.50	92			
		0.49	0.50	97	95	3.54	3.74
				OVERALL:	101	9.02	8.98

Table II-10. Continuing quality control data (duplicate matrix spikes) for the methyl parathion field study.

Study: 107
Analyte: Methyl paraoxon
MDL: 0.10 ppb
Date of Report: 7/10/91

Sample Type: Surface Water
Lab: Enseco- Cal Analytical
Chemist: Calvin Tanaka

Extraction Set Sample No.'s	Lab #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
1002, 1038	58126	0.65	0.50	131			
		0.68	0.50	137	134	4.24	3.17
1013	58232	0.41	0.50	82			
		0.48	0.50	96	89	9.9	11
2013, 2038	58383	0.55	0.50	109			
		0.58	0.50	115	112	4.24	3.79
3033, 4023, 4033	58577	0.47	0.50	94			
		0.46	0.50	91	93	2.1	2.3
2023, 3003, 4003	58446	0.56	0.50	112			
		0.59	0.50	117	115	3.54	3.09
5007	58676	0.49	0.50	99			
		0.52	0.50	104	102	3.54	3.48
				OVERALL:	107	16.3	15.2

Table II-11. Results of the split sample analyses for methyl parathion concentrations from Enseco-Cal (CAL), the quality control laboratory and the California Department of Food and Agriculture, Chemistry Laboratory Services (CDFA), the primary laboratory.

CAL (µg/L)	CDFA (µg/L)
180.00	162.20
230.00	214.20
120.00	111.00
49.00	51.27
52.00	38.22
48.00	50.07
28.00	22.27
38.00	52.83
12.00	15.81
8.00	6.94
4.40	2.95
0.80	0.72
4.20	3.76
4.00	3.11
2.40	1.90
0.37	0.26
0.20	0.10
0.82	1.00

Regression Results:

Intercept	Prob>F	Slope	Prob>F
1.07	0.52	0.919	0.001

Source of Variation	Degrees of Freedom	Mean Squared Error	F-Value	P-Value
CDFA vs CAL	1	63901.5	1961.9	0.0001
Error	16	32.6		

Table II-12. Results of the split sample analyses for methyl paraoxon concentrations from Enseco-Cal (CAL), the quality control laboratory and the California Department of Food and Agriculture, Chemistry Laboratory Services (CDFA), the primary laboratory.

CAL (µg/L)	CDFA (µg/L)
0.38	0.25
0.92	0.52
0.27	0.25
1.30	0.66
0.99	0.44
1.30	0.72
2.10	0.39
0.31	0.33

Regression Results:

Source of Variation	Degrees of Freedom	Mean Squared Error	F-Value	P-Value
CDFA vs CAL	1	0.06472	2.504	0.1647
Error	6	0.02585		

APPENDIX III

Field Data and Sampling Results

Table III-1. Field 1 data and concentrations of methyl parathion (MP) and methyl paraoxon (MPox) found after application.

DAA[a]	Water Depth	Water Temp.	pH	MP (µg/L)	MP (kg/ha)	MPox (µg/L)
2[b]	19.2	17.6	7.1	142.12 100.48 121.30 ± 29.444	0.23290	0.50 0.33 0.42 ± 0.120
3	18.8	18.1	7.1	66.42 75.34 70.88 ± 6.307	0.13297	0.29 0.29 0.29 ± 0.0
4	18.4	18.8	6.9	51.27 35.89 43.58 ± 10.875	0.08001	0.25 0.23 0.24 ± 0.014
5	17.3	18.2	7.1	33.93 41.08 37.51 ± 5.056	0.06475	0.20 0.23 0.22 ± 0.012
7	16.9	17.4	7.4	15.81 12.43 14.12 ± 2.390	0.02381	0.12 0.078 0.01 ± 0.029
9	13.5	12.4	7.5	6.19 5.99 6.09 ± 0.141	0.00820	<0.05 <0.05 <0.05
11	13.1	13.5	7.2	3.11 3.38 3.25 ± 0.191	0.00425	<0.05 <0.05 <0.05
15	10.1	18.4	7.2	1.37 2.40 1.89 ± 0.728	0.00190	<0.05 <0.05 <0.05
19	8.8	18.3	6.8	0.51 0.56 0.54 ± 0.035	0.00047	<0.05 <0.05 <0.05
23	11.3	30.3	7.5	0.35 0.24 0.30 ± 0.078	0.00034	<0.05 <0.05 <0.05

a - Day after application
b - Methyl parathion and methyl paraoxon concentrations are questionable due to contamination during the blow down step of the analytical method.

Table III-2. Field 2 data and concentrations of methyl parathion (MP) and methyl paraoxon (MPox) found after application.

DAA[a]	Water Depth	Water Temp.	ph	MP (µg/L)	MP (kg/ha)	MPox (µg/L)
2	9.0	13.6	7.2	162.2 162.0 162.1 ± 0.141	0.14602	0.52 0.63 0.58 ± 0.078
3	8.6	17.9	7.2	89.17 83.41 86.29 ± 4.073	0.07428	0.36 0.21 0.29 ± 0.106
4	8.1	28.0	7.2	38.22 36.61 37.42 ± 1.138	0.03034	0.25 0.28 0.27 ± 0.021
5	6.9	23.4	6.9	17.96 18.59 18.28 ± 0.445	0.01262	0.13 0.12 0.13 ± 0.007
7	5.6	13.0	6.9	6.94 6.62 6.78 ± 0.226	0.00380	<0.05 <0.05 <0.05
9	7.8	34.1	7.1	7.41 6.87 7.14 ± 0.382	0.00557	0.10 0.09 0.10 ± 0.007
11	4.5	22.6	7.0	1.90 2.37 2.14 ± 0.332	0.00096	<0.05 <0.05 <0.05
15	4.3	27.6	8.1	0.70 0.64 0.67 ± 0.042	0.00029	<0.05 <0.05 <0.05

a - Day after application.

Table III-3. Field 3 data and concentrations of methyl parathion (MP) and methyl paraoxon (MPox) found after application.

DAA[a]	Water Depth	Water Temp.	ph	MP (µg/L)	MP (kg/ha)	MPox (µg/L)
2	13.8	15.9	7.7	214.2 194.0 204.10 ± 14.284	0.27969	0.66 0.71 0.69 ± 0.035
3	13.3	24.5	8.0	58.02 102.20 80.11 ± 31.240	0.10580	0.38 0.69 0.54 ± 0.219
4	12.9	25.5	8.0	50.07 23.60 36.84 ± 18.717	0.04719	0.44 0.28 0.36 ± 0.113
5	13.2	33.5	7.9	22.13 7.65 14.89 ± 10.239	0.0152	0.30 0.15 0.23 ± 0.106
7	12.0	25.5	7.4	2.95 1.41 2.18 ± 1.089	0.00260	0.06 <0.05 0.06
9	10.1	18.5	8.0	1.05 0.48 0.77 ± 0.403	0.00077	<0.05 <0.05 <0.05
11	9.5	19.8	7.7	0.26 0.48 0.37 ± 0.156	0.00035	<0.05 <0.05 <0.05
15	7.3	26.8	8.6	0.17 0.22 0.20 ± 0.035	0.00014	<0.05 <0.05 <0.05
23	3.9	27.2	8.3	0.06 <0.05 0.06	0.00002	<0.05 <0.05 <0.05

a - Day after application.

Table III-4. Field 4 data and concentrations of methyl parathion (MP) and methyl paraoxon (MPox) found after application.

a DAA	Water Depth	Water Temp.	ph	MP (µg/L)	MP (kg/ha)	MPox (µg/L)
2	11.8	19.0	9.4	111.00 123.50 117.25 ± 8.839	0.14127	0.72 0.77 0.75 ± 0.035
3	11.4	28.6	9.0	54.03 58.04 56.04 ± 2.836	0.06523	0.78 0.72 0.75 ± 0.042
4	10.4	19.6	8.3	22.27 35.18 28.73 ± 9.129	0.03051	0.39 0.49 0.44 ± 0.071
5	10.7	24.9	8.4	5.97 7.30 6.64 ± 0.940	0.00725	0.16 0.20 0.18 ± 0.028
7	8.8	23.3	7.8	0.72 0.52 0.62 ± 0.141	0.00056	<0.05 <0.05 <0.05
9	6.1	21.7	8.2	0.19 0.22 0.21 ± 0.021	0.00013	<0.05 <0.05 <0.05
11	7.1	24.1	8.0	0.10 0.13 0.12 ± 0.021	0.00009	<0.05 <0.05 <0.05
15	3.3	29.2	8.6	0.10 0.09 0.10 ± 0.007	0.00003	<0.05 <0.05 <0.05
23	6.8	29.3	8.3	<0.05 <0.05 <0.05	<0.00003	<0.05 <0.05 <0.05

a - Day after application.

Table III-5. Field 5 data and concentrations of methyl parathion (MP) and methyl paraoxon (MPox) found after application.

a DAA	Water Depth	Water Temp.	ph	MP (µg/L)	MP (kg/ha)	MPox (µg/L)
3	9.5	17.6	7.8	72.11 60.74 66.43 ± 8.040	0.06354	0.70 0.76 0.73 ± 0.042
4	14.1	19.5	8.2	52.83 36.23 44.53 ± 11.738	0.06321	0.33 0.15 0.24 ± 0.127
5	12.6	22.1	7.7	23.29 20.16 21.73 ± 2.213	0.02757	0.15 0.13 0.14 ± 0.014
7	11.1	27.5	7.8	3.76 4.32 4.04 ± 0.396	0.00451	<0.05 <0.05 <0.05
9	5.3	21.9	7.8	1.37 0.77 1.07 ± 0.424	0.00057	<0.05 <0.05 <0.05
11	8.2	23.8	7.7	1.00 0.68 0.84 ± 0.226	0.00069	<0.05 <0.05 <0.05
15	7.3	28.2	7.6	0.20 0.20 0.20 ± 0.0	0.00015	<0.05 <0.05 <0.05
19	9.1	23.2	7.7	0.34 0.15 0.25 ± 0.134	0.00023	<0.05 <0.05 <0.05
23	6.8	24.1	8.0	<0.05 <0.05 <0.05	<0.00003	<0.05 <0.05 <0.05

a - Day after application.